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GEOCHEMICAL MODELLING RELEVANT TO ONTARIO HYDRO'S WASTE DISPOSAL PROGRAMS

Report No. 88-317-K

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ABSTRACT

A geochemical modelling effort has been initiated to evaluate and predict the geochemical processes operating in various waste disposal systems. The examples chosen here represent a wide range of geochemical problems that are directly relevant to Ontario Hydro's waste management programs. Specifically, we have attempted to demonstrate the wide applicability of the geochemical computer program PHREEQE to geochemically diverse problems such as the evaluation of FGD waste leaching, leachate/clay liner interactions, bedrock gypsum dissolution as related to the R.H. Saunders G.S. dam safety program, grout carbonation for the C-14 isolation research program, and oxidation-induced changes in anoxic leachates from a low-level radioactive waste disposal site in the U.S.

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GEOCHEMICAL MODELLING RELEVANT TO ONTARIO HYDRO'S WASTE DISPOSAL PROGRAMS

1.0 INTRODUCTION

As the largest utility in Canada, Ontario Hydro has, in the process of generating electricity, produced large amounts of both radioactive and non-radioactive wastes. Although most of these wastes are presently in storage at the BNPD site and the thermal generating stations, various disposal options are under consideration. Regardless of the disposal options being evaluated, it is imperative that the long-term environmental impact of the waste on the site and ambient groundwater quality be assessed.

Normally, laboratory tests are performed to identify the important factors and conditions affecting the geochemical behaviour of the waste materials. However, such tests alone cannot generate adequate information to predict field behaviour and long-term effects of the waste at the disposal site.

Geochemical modelling, on the other hand, can be used to obtain such information provided the geochemical environments and waste properties are correctly documented. The success and effectiveness of geochemical modelling depends largely on the modeller's understanding of and insights into the geochemical system under consideration. In most cases, modelling provides a logical explanation of observed laboratory and field data, and from there predicts what would happen should conditions change at the disposal site.

In this report, we present a few cases in which geochemical computer programs can be used to explain and predict the geochemical processes operating in various waste disposal systems. The examples are chosen to represent a wide range of geochemical problems that are directly relevant to Ontario Hydro's waste management programs. The emphasis here is to demonstrate the wide applicability of geochemical modelling to diverse waste disposal problems rather than to give exact solution to the individual problems involved.

As part of this initiative in the Civil Research Department, geochemical computer programs have been acquired from the U.S. Nuclear Regulatory Commission, Canadian Centre for Inland Waters in Burlington, and the Universities of Waterloo and Western Ontario. These programs include PHREEQE, WATEQF, MINTEQ, and GEOCHEM. Since PHREEQE (Parkhurst et al, 1980) has been shown useful in the modelling of waste disposal problems (INTERA, 1983), we have attempted to demonstrate in this report its applicability to geochemical problems relevant to Ontario Hydro's needs.

The aqueous solution submodels in PHREEQE can calculate such thermodynamically important quantities as free ion activities from measured chemical compositions of a solution. Geochemical reaction submodels in this program describe changes in the chemistry of solutions and associated solids which occur as reactions proceed. Such reactions may be brought about by mixing of two solutions, adding solid material to a solution, or by changing the temperature of a solution or a solution with a solid. PHREEQE follows these reactions by the mass transfer principle, and calculates the masses of phases dissolved or precipitated and the associated fluid composition resulting from user-specified reaction steps and phase assemblages. A full account of chemical submodels and numerical methods used in PHREEQE is beyond the scope of this report and the readers are referred to the User's Manual (Parkhurst et al., 1980).

The most common application of PHREEQE is in the determination of speciation of the solution and saturation indices of the minerals. PHREEQE can compute the activity of the complexed and uncomplexed cationic and anionic species, neutral ion-pairs, and the distribution of both cationic and anionic species among their redox states. The solubility submodels then calculate and compare these ion activity products (IAP) to the solubility products (KT) for the minerals and solid phases stored in the thermodynamic data base. This comparison of the ion activity product to mineral solubility product evaluates whether certain dissolved constituents in the aqueous solution are in equilibrium with particular solid phases. If this solution is computed to be at equilibrium [Log(IAP/KT)=0] with a particular solid phase, then it is possible that the solid is precipitating or dissolving at a sufficient rate for it to be controlling the concentration of certain constituents in the solution. If the solution is computed to be oversaturated [Log(IAP/KT)>0] with a certain solid phase, then it is inferred that kinetic and/or mineralogical factors usually prevent precipitation of the solid phase. In some cases, certain elements may be complexed by organic compounds in the solution. This may lead to apparent oversaturation of certain solid phases, because organic complexation is not considered in the current data base of PHREEQE.

The thermodynamic data base attached to PHREEQE has been revised and expanded by Crowe (1986). This revised data base has been used in our modelling effort. Clay minerals are usually excluded from the data base because their chemistry and mineralogy are complex and, as a result, their thermodynamic properties are not well documented. However, interactions between soil clay minerals and waste leachates are important considerations in waste disposal problems. Therefore, in our modelling effort, we use the revised thermodynamic data on clay minerals by Grambow (1986).

As part of this study, we have considered several waste disposal systems, covering a wide range of geochemistries that reflect differences not only in

waste characteristics but also in the underlying geochemical processes which contribute to leachate generation, the resultant leachate chemistry and the geochemical environment. Specifically, several test cases have been selected for our modelling effort to evaluate flue gas desulphurization (FGD) waste leaching behaviour and temporal changes in waste leachate chemistry, leachate/clay liner interactions, gypsum dissolution and the effect of salt concentration and redox conditions on gypsum and anhydrite solubility, grout carbonation and evolving water chemistry and mineralogy, and oxidation-induced changes in anoxic leachates from a low-level radioactive waste disposal site.

2.0 FGD WASTE LEACHING AND CLAY LINER INTERACTIONS

Flue gas desulphurization is a viable method to control SO_x emissions from coal-fired generating stations. Ontario Hydro has conducted pilot-scale studies at Lakeview T.G.S. to evaluate the dry limestone injection process. Preliminary characterization of FGD waste generated from this process has been carried out by Golomb (1987).

More recently, an investigation of the geochemical properties and leaching behaviour of FGD wastes relevant to field disposal conditions has been initiated in the Civil Research Department (Zhou and Dayal, 1988a). This study will generate important information for the assessment of the long-term environmental impact of FGD waste disposal.

2.1 FGD WASTE LEACHING BEHAVIOUR

Given the field conditions and waste properties, the geochemical behaviour of the waste material at a disposal site can be predicted using PHREEQE. In the case of solid dissolution, PHREEQE can simulate leachate chemistry in the course of dissolution, with or without precipitation reactions. At present, however, the available data on the chemical properties and leaching characteristics of Ontario Hydro's FGD waste by-product are not adequate. Therefore, only preliminary modelling can be performed at this time.

We have modelled the dissolution behaviour of three FGD waste samples from Lakeview TGS generated during a pilot test run in July/August 1987. The chemical composition of the waste materials are shown in Table 2.1. The important constituents considered for the dissolution reactions are Ca^{2+}, CO_3^{2-} and SO_4^{2-}. This is based on the following considerations: a) calcium hydroxide, calcium carbonate and calcium sulphate are the major phases of FGD waste; and b) other components in FGD waste are associated with fly ash and exhibit a much slower dissolution rate than the calcium minerals. Since only congruent dissolution is considered here, the silicate minerals have been excluded from the calculations.

Our modelling results indicate that the three Lakeview samples designated as LIF-1, LIF-2, and LIF-3 (based on direct limestone into the furnace) are similar in their dissolution behaviour. Table 2.2 shows the modelling results of incremental dissolution of LIF-2. Apparently, LIF waste leachate is very alkaline, showing initial saturation with respect to calcite. Because adequate data are not available on the leaching properties of our own LIF waste, detailed modelling would be of little value since simulation of the leaching behaviour cannot be

verified. However, the data provided by Constable et al (1988) on FGD waste leaching is relatively complete and has been selected for more detailed modelling of the dissolution behaviour.

Table 2.1 Chemical Composition of Lakeview LIF Wastes[1]

Components	LIF-1(%)	LIF-2(%)	LIF-3(%)
Al_2O_3	9.26	11.90	11.33
BaO	0.04	0.06	0.05
CaO	39.06	33.60	38.78
Fe_2O_3	8.86	12.71	7.71
K_2O	0.84	1.21	0.96
MgO	3.36	1.09	0.49
MnO	0.02	0.02	0.02
Na_2O	0.31	0.36	0.35
SrO	0.09	0.10	0.10
TiO_2	0.42	0.55	0.53
CO_2	5.94	4.20	2.89
SO_3	6.58	5.13	5.78
Unburnt Carbon	3.70	3.24	1.96
TOTAL	78.33	73.99	70.77

[1] SiO_2 concentrations are not available at this time.

The FGD waste materials, studied by Constable et al. (1988), are derived from Queen's University Pilot Plant in Kingston, Ontario, and the full-scale unit at Canadian Forces Base (CFB) in Summerside, Prince Edward Island. Laboratory tests were performed at the Wastewater Technology Centre (Environment Canada) to evaluate the leaching properties of the waste materials. The laboratory results indicate that the leachates are highly alkaline (pH = 10.0 to 12.5), with a high total dissolved solids content. The major constituents in the leachates are calcium and sulphate, with minor amounts of chloride, sodium, potassium, fluoride, silicon, aluminum, and strontium. Calcium and sulphate concentrations are usually several orders of magnitude greater than the other leached constituents. The releases of Ca^{2+} and SO_4^{2-} in the batch and column tests are shown in Figures 2.1 and 2.2.

Modelling is performed only on the dissolution of Summerside FGD waste material. Its chemical composition is reported in Constable et al (1988). In our first simulation, a net stoichiometric solid reactant was added to the leachant in five

Table 2.2 Simulation of LIF Waste Dissolution Behaviour (No Solubility Control)

Moles of Reaction[1]	pH	Total Dissolved Elements (mmol)			Saturation Indices (log IAP/KT)			
		Ca	C	S	Calcite	Gypsum	Anhydrite	Portlandite
0.01	11.85	5.89	0.95	0.67	2.17	-1.32	-1.64	-1.41
0.02	12.12	11.78	1.90	1.34	2.51	-0.87	-1.19	-0.67
0.03	12.27	17.67	2.85	2.01	2.70	-0.62	-0.95	-0.25
0.04	12.38	23.56	3.80	2.68	2.84	-0.45	-0.78	0.05
0.05	12.47	29.45	4.75	3.35	2.94	-0.33	-0.65	0.27

[1]Represents simulation of dissolution behaviour based on incremental addition of waste reactant to a constant volume of leachant.

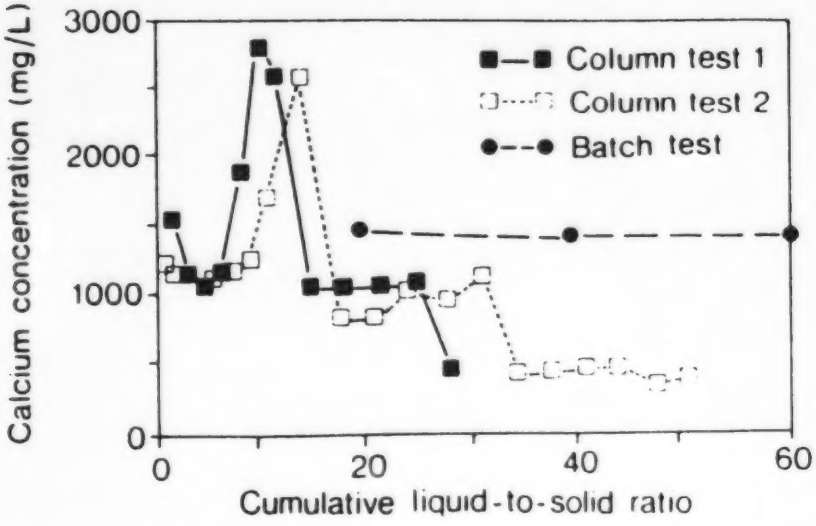

Fig 2.1. Ca^{2+} concentrations in batch and column FGD waste leachates (Constable et al., 1988)

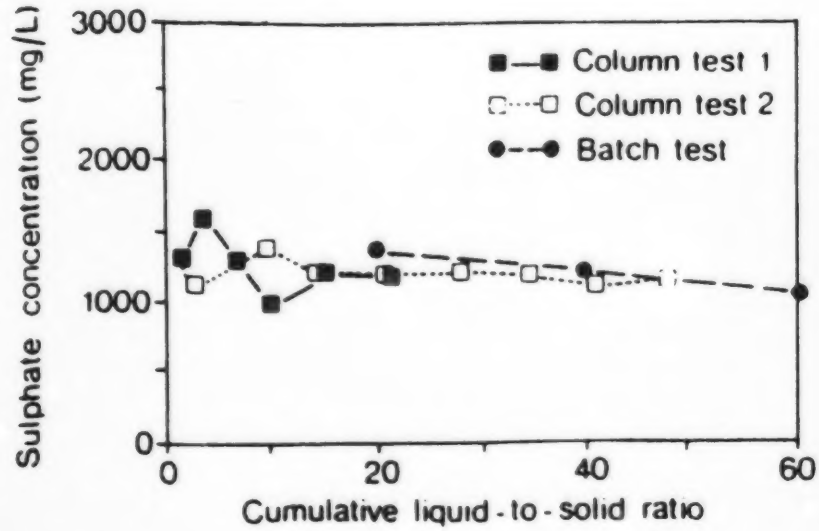

Fig 2.2. SO_4^{2-} concentrations in batch and column FGD waste leachates (Constable et al., 1988)

equal increments, assuming no solubility control by any solid phase. As shown in Table 2.3, modelling results indicate that the waste leachate will be highly alkaline (pH>12.0), which is consistent with the experimental results of Constable et al (1988). However, the leachate is oversaturated with respect to both gypsum and portlandite after 0.03 moles of reactant were added to solution. Because no precipitation was considered in this particular case, both Ca^{2+} and SO_4^{2-} concentrations in the leachates increase linearly with amount of reactant added. This is, of course, not in agreement with the experimental results which show no such linear relationship, indicating that some solid phases must be controlling the leachate chemistry.

Further modelling was performed to evaluate the control the solid phases are likely to exert on leachate chemistry. Because $CaSO_4$ and CaO are the dominant phases in the Summerside FGD waste (Constable et al., 1988) and CaO is readily transformed to $Ca(OH)_2$ upon contact with water, anhydrite and portlandite would be the dominant solid phases expected to exert control on leachate chemistry. Gypsum was also considered because it is a more stable phase than anhydrite in the system involved. Calcium carbonate minerals were not considered because the carbonate contents of the waste itself, as well as the dissolved inorganic carbon and alkalinity of the leachates, were not reported.

Simulated solution chemistry of the leachates equilibrated with solid phases are shown in Table 2.4. No further dissolution should occur after the leachates reach saturation with respect to anhydrite and portlandite at the same time. This leachate will contain 1288.5 mg/l of Ca^{2+} and 1308.5 mg/l of SO_4^{2-} (Table 2.4). These values are close to the Ca^{2+} and SO_4^{2-} concentrations of the initial leachate samplings of the column tests (Fig 2.1, 2.2), indicating that the dissolution reaction may be fast and a transient equilibrium was achieved in the experiments. This leachate, however, is oversaturated with respect to gypsum.

Gypsum may precipitate out from the leachate solution and this would lead to further dissolution of the waste material. If gypsum precipitation is fast relative to the dissolution of the waste, the Ca^{2+} and SO_4^{2-} concentration would decrease until the leachate is no longer oversaturated with respect to gypsum. This may explain why Ca^{2+} and SO_4^{2-} exhibited a steady decrease with time in experiments performed by Constable et al. (1988) [Fig. 2.1, 2.2].

A peak is observed in the Ca data for the column tests (Figure 2.1). Constable et al. (1988) do not provide any explanation for this anomaly. A corresponding peak is not present for SO_4^{2-}. The Ca peak in Figure 2.1 cannot be attributed to solubility control by the dominant mineral phases in the waste material. The observed anomaly in the calcium leaching behaviour may be a result of enhanced leaching at a higher temperature, due to incomplete slaking of the waste material used in the column tests.

In summary, the modelling results of FGD waste dissolution indicate that the evolving leachate chemistry with time can be predicted. Furthermore, the leachates will be highly alkaline, with solid phases exerting a strong control on leachate chemistry and that liner materials may be necessary to control leachate contamination of the ambient groundwater.

Table 2.3 Simulation of Summerside FGD Waste Dissolution Behaviour (No Solubility Control)

Moles of[1] Reaction	pH	Total Dissolved Elements (mmol)		Saturation Indices (log IAP/KT)		
		Ca	S	Gypsum	Anhydrite	Portlandite
0.01	12.0	10.2	3.1	-0.5016	-0.8272	-0.8334
0.02	12.3	20.4	6.3	-0.0822	-0.4075	-0.1179
0.03	12.4	30.6	9.4	0.1498	-0.1751	-0.2849
0.04	12.5	40.8	12.6	0.3092	-0.0154	0.5645
0.05	12.6	51.0	15.7	0.4302	0.1060	0.7786

[1]Represents simulation of dissolution behaviour based on incremental addition of waste reactant to a constant volume of leachant.

Table 2.4 Simulation of Summerside FGD Waste Dissolution Behaviour (With Solubility Control)

Controlling Solid Phase	pH	Ca^{2+} (mg/l)	SO_4^{2-} (mg/l)	Saturation Indices (log IAP/KT)		
				Gypsum	Anhydrite	Portlandite
Gypsum	12.2	932.2	684.5	0.0000	-0.3300	-0.1729
Anhydrite	12.4	1650.4	1223.5	0.3245	0.0000	0.3893
Portlandite	12.3	1102.0	816.9	0.0971	-0.2279	0.0000
Gypsum + Portlandite	12.3	1042.8	657.6	0.0000	-0.3300	0.0000
Anhydrite + Portlandite	12.3	1288.5	1308.5	0.3249	0.0000	0.0000

2.2 FGD Waste Leachate/Clay Liner Interactions

Further modelling was performed to evaluate the interactions between FGD waste leachate and soil clay minerals to identify liner materials that are compatible with the alkaline FGD waste leachate.

The interactions between FGD waste leachate and liner materials can be evaluated by geochemical modelling, provided the leachate chemistry is known. As a starting point, we calculate the saturation indices for common rock-forming minerals and clay minerals. For this simulation, we assumed the leachate chemistry to be controlled by gypsum and portlandite. Small amounts of K^+, Na^+, and Mg^{2+} and dissolved inorganic carbon are added to the system for modelling purposes. The modelling was performed in a system closed to or open to the atmosphere (PCO_2=$10^{-3.5}$; PO_2=$10^{-0.7}$).

The modelling results are shown in Table 2.5. When closed to atmospheric CO_2 and O_2, the FGD leachates are undersaturated, relative to the major rock-forming minerals (quartz, plagioclase, orthoclase, etc.) and Al-rich clay minerals (kaolinite, gibbsite, muscovite, illite, montmorillonite). This is reasonable because the leachate is highly alkaline and both Si and Al will be susceptible to chemical attack. Therefore, the common rock-forming minerals and some clay minerals are not stable and may undergo slow dissolution upon contact with alkaline FGD leachates. On the other hand, the FGD leachates are oversaturated relative to Fe- and Mg-rich clays (chlorites, nontronite, and saponite) and these could serve as suitable liner materials at a waste disposal site, keeping in mind that the PHREEQE simulations of leachate/clay liner interactions are based on limited thermodynamic data base for clay minerals.

When FGD leachate reacts with atmospheric CO_2 and O_2, solution pH decreases by 3 units, with an increase in solution Eh. The decrease in pH is due to an increase in dissolved CO_2 in the solution. As a result of such a change, the solution becomes saturated with almost all of the rock-forming minerals and clay minerals. The conclusion, of course, is based on the hypothetical composition of the leachate and assuming equilibrium with atmospheric CO_2 and O_2. The computer simulation of FGD waste leaching behaviour and leachate/clay liner interactions can be validated by comparing with actual field data from a FGD disposal site.

3.0 EVALUATION OF GYPSUM DISSOLUTION AND SOLUBILITY

Dissolution of gypsum and the resultant void development in the foundation rock at the R.H. Saunders GS dam has been of concern with respect to the structural stability of the dam. An investigation is underway in the Civil Research Department to determine the physical and chemical processes contributing to gypsum dissolution at the site (Zhou and Dayal, 1988b). As discussed in the paper by James and Lupton (1978), the rate of gypsum dissolution is controlled primarily by the surface area in contact with the water, the flow velocity of water past a unit area of the gypsum, and groundwater chemistry. This has been formulated by James and Lupton (1978) as:

Table 2.5. Saturation Indices Relative to Major Minerals for FGD Waste Leachate*

PHASE	LOG KT	Closed to Atmosphere LOG IAP/KT*	Open to Atmosphere LOG IAP/KT*
CALCITE	-8.4800	1.2680	3.3320
DOLOMITE	-17.0000	-2.4705	2.2816
SIDERITE	-10.5400	-16.5279	-11.8904
MAGNESITE	-8.2000	-4.0584	-1.3705
GYPSUM	-4.6060	-0.0061	-0.0606
ANHYDRITE	-4.2800	-0.3311	-0.3858
QUARTZ	-3.9300	-2.1045	0.8443
ALBITE L	3.1100	-8.0228	0.8380
ALBITE H	4.4300	-9.3428	-0.4820
ANORTHITE	27.0900	-2.6129	3.2021
MICROCLINE	0.7300	-5.6491	3.2129
PORTLANDITE	-5.4200	-0.0006	-6.0503
GIBBSITE	-33.8700	-1.1176	1.8362
BOEHMITE	7.9330	-0.9502	2.0336
CHALCEDY	-3.5230	-2.5115	0.4373
$SIO_2(AM)$	-2.7100	-3.3245	-0.3757
$FE(OH)_3AM$	4.8900	1.1391	1.9510
KAOLINITE	5.7300	-3.8337	8.0313
MUSCOVITE	12.9900	-3.9434	10.8861
NA-NONTRONITE	11.5600	8.7275	21.1780
K-NONTRONITE	10.5100	9.7754	22.2263
CA-NONTRONITE	5.1700	16.8398	29.2598
ILLITE	12.1200	-9.0759	4.9700
SAPONITE	34.9000	1.5957	-1.2510
CHLORITE	66.7400	16.7884	4.4724
MONTMORILLONITE	8.6200	-10.6578	6.0877

* The leachate was pre-saturated with both gypsum and portlandite

$$dM/dt = K*A*(Cs-C) \quad (1)$$

where M - mass of gypsum dissolved at time t,

C_s - equilibrium concentration,

C - dissolved gypsum concentration in solution at time t,

A - area of gypsum exposed to aqueous solution,

K - rate constant of dissolution.

Surface area, A, for a given system has to be determined in the field or estimated. The dissolution rate constant, K, is normally determined experimentally. (C_s-C) is a measure of the degree of undersaturation of ambient groundwater, relative to gypsum solubility. Equilibrium concentration, C_s, varies, depending on solution chemistry, temperature, and pressure. This concentration can be defined by geochemical models and would require concentration data for all major chemical constituents in the groundwater. This indicates that a complete geochemical analysis is required to evaluate the degree of undersaturation of groundwater and to determine the dissolution rate of gypsum.

Evaluation of existing geochemical data from the R.H. Saunders G.S. site, provided by A.R. Bennett of Civil Works Department, has been carried out. Unfortunately, the water chemistry data accumulated during the past years are incomplete and, therefore, inadequate for geochemical evaluation of gypsum dissolution at the site.

One water sample, recently taken by Civil Research from borehole SM-6 at the R.H. Saunders GS site, has been analyzed for all major components, and the analytical data (Table 3.1) has been used to define its geochemical character using PHREEQE. It is found that this particular sample is saturated with respect to gypsum (Table 3.2). At the time of sampling, however, the water sample imparted a strong H_2S odour, indicating strongly reducing conditions. By the time the sample was analyzed, all the H_2S had escaped and S^{2-} oxidized to SO_4^{2-}. This is also evident from the below detection levels of dissolved sulphate (Table 3.1).

Oxidation of the sample not only increased the SO_4^{2-} concentration but also changed the redox condition of the system. Both oxidation-induced changes result in an increase in the degree of saturation, relative to gypsum. Nevertheless, the solution is still found to be close to gypsum saturation, even though we assumed the sulphate concentration to be half of the observed value (Table 3.2). For subsequent water sampling, appropriate precautions will have to be taken to prevent oxidation of the water sample.

PHREEQE can compute the gypsum solubility dependence on temperature, gas pressure (e.g. PCO_2), and solution chemistry. As an example, we show here the solubility dependence on the sodium chloride concentration of a solution. It was reported that the rate of dissolution of gypsum and anhydrite increases with increasing concentration of sodium chloride in solution (James and Lupton, 1978). The effect of sodium chloride concentration in groundwater on gypsum and anhydrite

solubility was modelled by PHREEQE. The modelling was performed using two different approaches.

Table 3.1 Chemical Composition of SM-6 Water Sample

Constituents	Concentration (ppm)
Ca^{2+}	500
Mg^{2+}	115
K^{+}	15.7
Na^{+}	232
Sr^{2+}	10
SiO_2[1]	14.6
SO_4^{2-}	1800
Cl^{-}	174
DIC[2]	21
DOC[3]	<0.5
H_2S	<0.02

[1]Dissolved silica
[2]Dissolved inorganic carbon
[3]Dissolved organic carbon

Table 3.2. Saturation State of SM-6 Water Sample with Respect to Gypsum and Anhydrite

Mineral	Log (KT)[1]	Log (IAP/KT)[2] X	Log (IAP/KT)[2] Y
Gypsum	-4.61	0.171	-0.155
Anhydrite	-4.28	0.083	-0.408

[1]Log (KT) is log of equilibrium constant, K, at 25°C.

[2]Log (IAP/KT) is saturation index. A positive value means oversaturation, a negative value means undersaturation; Y represents half of the sulphate content of the observed value (X).

First, the saturation indices of gypsum and anhydrite were calculated for varying contents of NaCl in solution. The Ca^{2+} and SO_4^{2-} concentrations of these solutions are assumed to be the same ($[Ca^{2+}] = SO_4^{2-}] = 1.0$ mM), while sodium chloride concentration varies from 0.00M to 0.51M. The range of sodium chloride concentration selected is the same as that reported in the experimental work of James and Lupton (1978). However, their highest NaCl concentration is not geochemically realistic and the submodels used in PHREEQE cannot be applied to solutions of very high ionic strength. The results of our model calculations are shown in Table 3.3. Even though the Ca^{2+} and SO_4^{2-} concentrations are the same in fresh water and NaCl solution, the saturation indices of gypsum and anhydrite decrease with increasing concentration of NaCl in solution (Fig 3.1). This means that the degree of undersaturation (C_s-C) will become greater as the salt content increases. Thus, the dissolution rate of gypsum and anhydrite will increase according to equation (1).

In the second simulation, we directly compute the solubility of gypsum and anhydrite in solutions with varying concentrations of NaCl (Table 3.4). The results show that the solubilities of gypsum and anhydrite increase two-fold from fresh water to 0.17M NaCl solution (Fig. 3.2). In the case of gypsum and anhydrite, the solubility is equal to the equilibrium concentration, C_s, in equation (1). Therefore, the C_s value in equation (1) will increase with increasing salt content, with a corresponding increase in the degree of undersaturation and, hence, the dissolution rate. Similarly, the effect of other ion species can also be calculated and predicted.

This simple example illustrates clearly that geochemical modelling can be used quite effectively for the gypsum dissolution problem, in particular, the definition of the geochemical character of ambient groundwater relative to gypsum dissolution; calculation of the dependence of solubility, degree of undersaturation and dissolution rate on solution chemistry; and simulation of incremental changes in solution chemistry induced as a result of gypsum dissolution.

All these geochemical factors and conditions are directly relevant to evaluation of the formation and subsequent enlargement of fissures and caverns in gypsiferous foundation rock which, in turn, can contribute to the overall instability of a hydraulic dam.

4.0 GROUT CARBONATION AND EVOLUTION OF RESULTANT WATER CHEMISTRY AND MINERALOGY

As part of the reactor operating waste disposal program underway at Ontario Hydro, laboratory experiments were performed by Moddle and Reardon (1988) at the University of Waterloo to study powdered grout/CO_2 interactions in aqueous medium, paying particular attention to the nature and extent of grout carbonation, as well as to the evolving mineral assemblage and water chemistry with increasing degree of carbonation.

This work is of direct relevance to Ontario Hydro's reactor waste backfill project in that it sheds light on the mechanics of grout carbonation which, in turn, is of importance to C-14 attenuation and immobilization in cement-based backfill materials. Secondly, prediction of stable end products and

Table 3.3 Effect of Sodium Chloride Concentration on Saturation Index of Gypsum & Anhydrite

NaCl Concentration (g/l)	Saturation Index of Gypsum	Saturation Index of Anhydrite
0	-1.6276	-1.9535
1	-1.8928	-2.2182
3	-2.1372	-2.4616
10	-2.5373	-2.8584
30	-3.0343	-3.3447

Table 3.4 Effect of Sodium Chloride Concentration on the Solubility of Gypsum and Anhydrite

NaCl Conc. (M)	Gypsum (M)	Anhydrite (M)
0.0000	0.0101	0.0169
0.0171	0.0116	0.0188
0.0513	0.0134	0.0219
0.1711	0.0202	0.0302

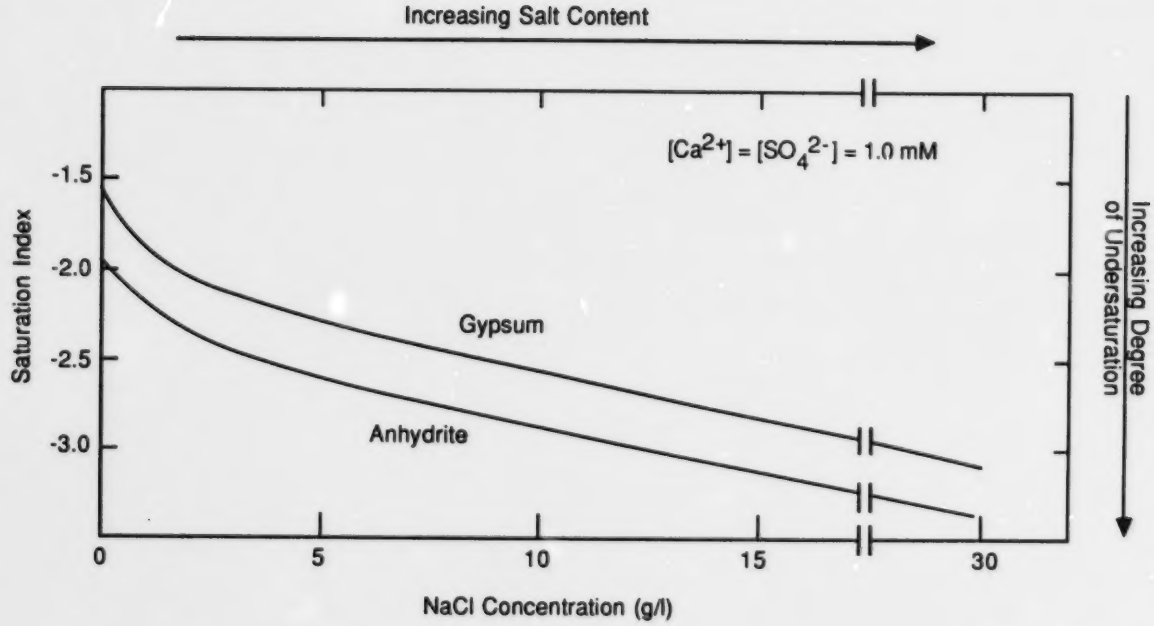

Fig 3.1. Effect of salt content of solution on the degree of saturation, relative to gypsum and anhydrite.

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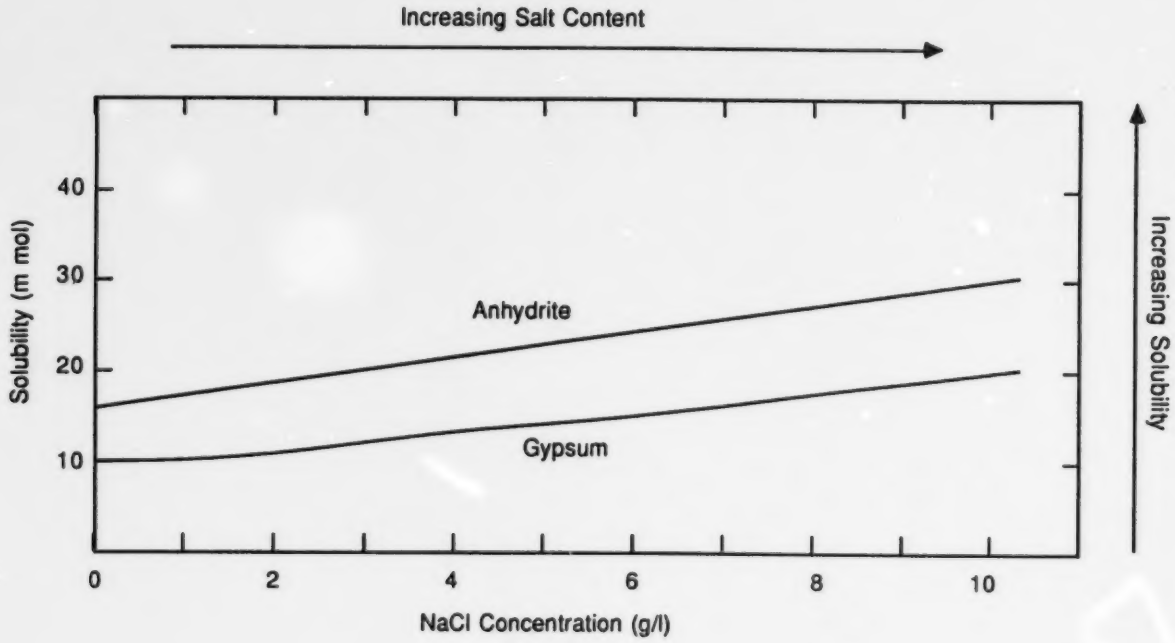

Fig. 3.2. Effect of salt content of solution on the solubilities of gypsum and anhydrite.

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establishment of resultant water chemistry provides further information on the long-term durability and stability of test materials.

Briefly, the grout material used in the University of Waterloo grout/water reaction experiments was formulated and prepared in the Civil Research Department at Ontario Hydro. The pulverized grout/water solutions were prepared using two different water/solid ratios; namely, 30g or 15g of solid in 240g of distilled water and subsequently equilibrated with three water-saturated gas mixtures : 1%, 5% and 100% CO_2(balance N_2).

The experimental results for the two solid/water experimental systems at varying levels of CO_2 concentrations are presented, in terms of the observed concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, SiO_2, SO_4^{2-}, dissolved inorganic carbon, pH, and conductivity, as a function of time (Moddle and Reardon, 1988). The results indicate that the carbonation reactions are characterized by the incongruent dissolution of grout mineral phases and precipitation of the reaction products, calcium carbonate and amorphous silica. Moddle and Reardon (1988) further report that under open conditions with respect to atmospheric CO_2, the carbonation reactions progress continuously until all available Ca-bearing grout phases have reacted.

Moddle and Reardon (1988) used PHREEQE to model geochemical reactions controlling grout/water/CO_2 interactions and to identify the mineral phases that are likely to exert control on the resultant water chemistry. The simulations further attempt to explain the extent of carbonation observed in the experimental runs.

Based on the simulation runs, three main stages of the carbonation sequence can be delineated:

- an initial stage, marked by small changes in pH and pCO_2 during grout dissolution.
- an intermediate stage, marked by sharp changes in pH and pCO_2.
- a final stage, characterized by an approach to constant pH and pCO_2.

Comparison of the pH data from the simulation and experimental runs helps to explain the extent of carbonation observed in the experimental runs. For example, in:

- 1% CO_2 system: solid materials are carbonated to completion (dominated by the carbonation of the solid phases).
- 5% CO_2 system: dominated by carbonation of the solution phase (drastic changes in pH).
- 100% of CO_2: full carbonation of the entire grout/water system approaching equilibrium, as reflected by constant pH values.

The predicted changes in mineral assemblage during the three stages of the simulation of grout/CO_2/water reactions are depicted in Fig. 4.1 and summarized as follows:

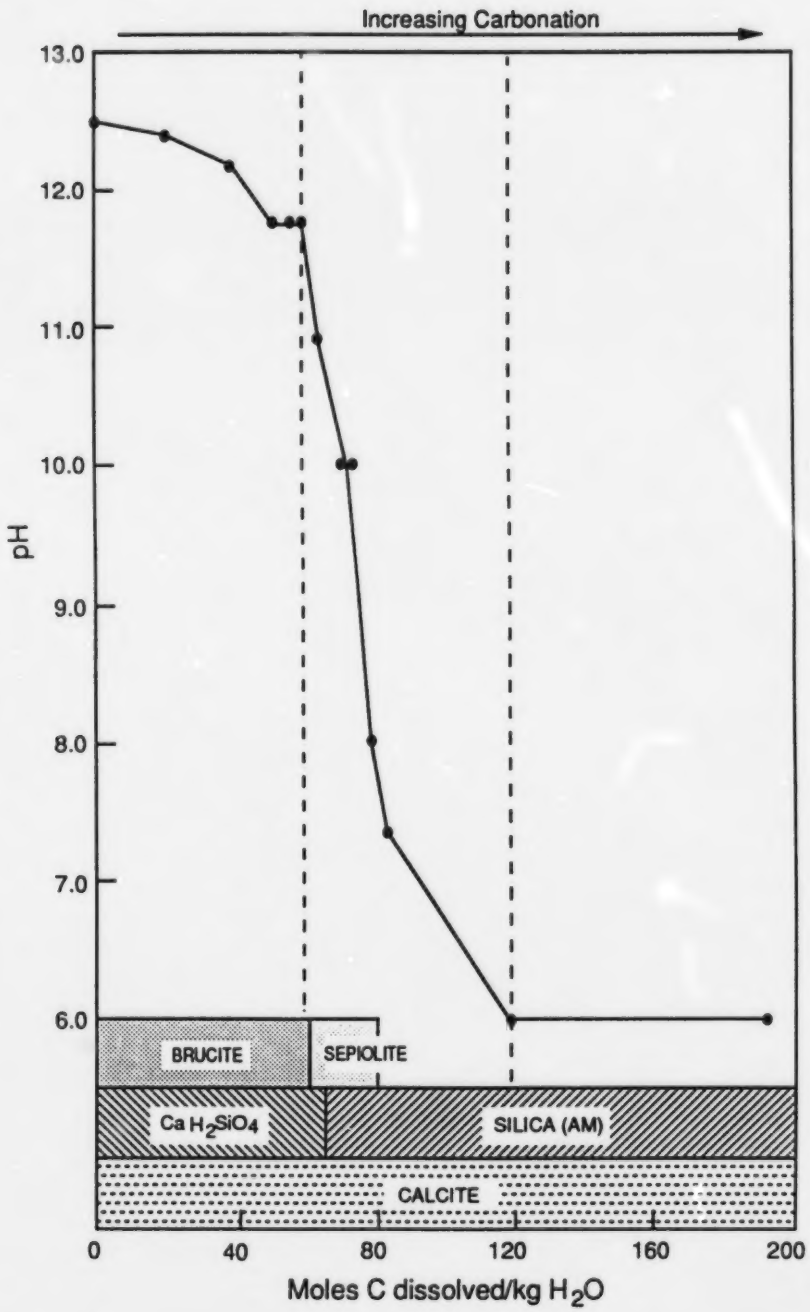
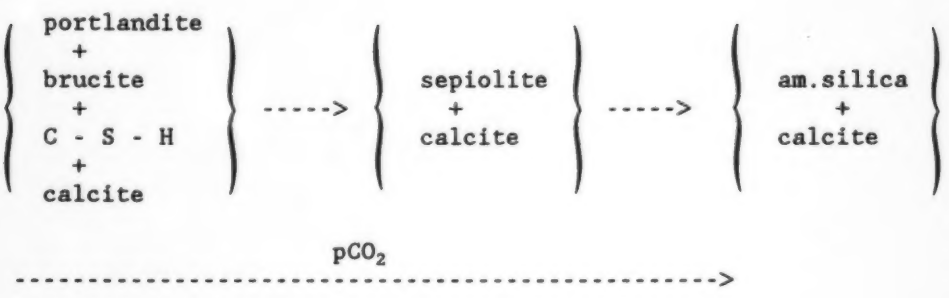


Fig. 4.1. Simulation of progressive carbonation reaction in a grout/water system, showing the predominant mineral phases exerting control on the evolving solution chemistry (after Moddle and Reardon, 1988).

Carbonation sequence



As evident from Fig. 4.1, the starting point for the grout/water carbonation reaction simulation is portlandite equilibrium. Upon addition of carbonic acid, however, this equilibrium is quickly disturbed, with brucite, calcium silicate, and calcite exerting control on the evolving water chemistry. Since both Ca^{2+} and CO_3^{2-} are predominant in the aqueous system, calcite stability is maintained throughout the simulation and will be omnipresent during the entire grout carbonation reaction.

According to Moddle and Reardon (1988), the dashed vertical line in Fig. 4.1 delineates the end of the initial phase of carbonation, indicating that the grout has been fully reacted. The intermediate phase is characterized by carbonation of the solution phase, as depicted by drastic changes in pH. During this carbonation phase, the solution initially exhibits equilibrium with respect to sepiolite and amorphous silica. However, with increasing degree of carbonation, the pH drops below 10 at which sepiolite is unstable. The final phase, reflecting complete carbonation, is characterized by the presence of stable end-products, amorphous silica and calcite, which exert control on the final solution chemistry.

In summary, the above simulation based on PHREEQE provides insights into the nature and extent of carbonation taking place in the experimental runs. For example, in the 1% CO_2 runs, the carbonation reaction progressed to the point at which the solid material was fully carbonated and, upon further addition of CO_2 (such as that in the 5% run), it is the solution phase that is being progressively carbonated as reflected in drastic decreases in pH. On the other hand, in the 100% CO_2 runs sufficient carbon was added to the aqueous system to result in rapid carbonation of both the solid and solution phases, corresponding to an accelerated carbonation process.

More recent work at the University of Waterloo is designed to evaluate the nature and extent of grout carbonation induced as a result of incremental additions of CO_2 to a grout/H_2O system (Daewele and Reardon, 1988). The data generated from these experiments will be more amenable to geochemical modelling for elucidation of the carbonation processes and end-products in the overall grout/CO_2/H_2O systems under investigation.

5.0 GEOCHEMISTRY OF TRENCH LEACHATES FROM MAXEY FLATS RADIOACTIVE WASTE DISPOSAL SITE

As part of the U.S. Nuclear Regulatory Commission efforts to develop a data base on source term characteristics for low-level radioactive wastes, a considerable amount of data has been generated on trench leachate chemistry for the commercially-operated shallow land burial sites located in the eastern United States (Barnwell, South Carolina; Maxey Flats, Kentucky; Sheffield, Illinois; and West Valley, New York). Studies of existing low-level waste disposal sites in the U.S. have provided a unique opportunity to investigate the behaviour and fate of radioactive waste nuclides in a natural setting, as well as to assess the performance of the waste package under field disposal conditions. In addition, the complete chemical analyses performed on all trench leachates sampled from the various sites provide an excellent opportunity to evaluate and validate existing geochemical models. In fact, the Maxey Flats data are being used by the European nuclear waste management community, as part of the CHEMVAL project, to evaluate existing geochemical models and their thermodynamic data bases (D. Atkins, pers. comm.).

For the purposes of our modelling effort in this report, we have selected the Maxey Flats trench leachate data to evaluate the geochemical controls on source term characteristics and the oxidation-induced changes in leachate chemistry.

The major features of the source term characterization studies for the Maxey Flats disposal site, as reported by Dayal et al (1984), are highlighted below.

A combination of hydrological and geochemical factors determines to a large extent the formation and compositions of the trench leachates. At the Maxey Flats site, the waste trenches are located in nonporous shale of low hydraulic conductivity. This results in accumulations of rainwater that infiltrates through the trench caps. Such accumulations of stagnant water and its eventual overflow have been termed the 'bathtub effect'. Because of the long residence time of the accumulated water in the trenches, prolonged leaching and microbial degradation of waste materials occur continuously, leading to leachate formation. As a result of such interactions for extended time periods, the resultant trench leachates exhibit significant modifications in terms of inorganic, organic, and radionuclide constituents and acquire geochemical properties that are unique, compared to ambient groundwater.

The leachates generally exhibit varying degrees of anoxia characterized by negative redox potentials, low dissolved oxygen and sulphate concentrations, high alkalinity, and high ammonia concentrations. The enrichments, to varying degrees, of inorganic, organic, and radionuclide constituents associated with fuel and non-fuel cycle low-level wastes reflect the nature of the leaching process itself and the waste materials. Elevated concentrations of Na^+, K^+, Fe_{total}, Cl^-, dissolved organic and inorganic carbon, and several organic compounds as well as radionuclides, such as ^{3}H, ^{241}Am, ^{60}Co, ^{134}Cs, ^{137}Cs, ^{90}Sr, ^{238}Pu, and $^{239,240}Pu$ are a consequence of waste leaching. Some of the waste-derived organic compounds present in the trenches, such as chelating agents and several carboxylic acids, are strong complexing agents and have the potential to form stable radionuclide complexes and thus enhance nuclide mobility.

5.1 Geochemical Controls on Trench Leachate Chemistry

In addition to waste leaching and microbial degradation reaction controls on trench leachate compositions, the leachate solutes are also subject to abiogenic precipitation reactions, especially in relatively stagnant systems such as those at Maxey Flats where the products of waste leaching and microbial degradation are continually generated and subsequently accumulate. To evaluate solubility controls on leachate chemistry, Dayal et al (1984) performed geochemical modelling using WATEQF for the calculation of saturation states of trench leachate solutes with respect to given mineral phases.

Figure 5.1 shows the calculated saturation indices (log IAP/KT) for the carbonate, sulphate, phosphate, fluoride, and sulphide minerals plotted for each trench leachate sample. The horizontal bars on either side of the equilibrium line (log IAP/KT = 0) represent 5% tolerance limits on saturation index values due to uncertainties in the values of mineral solubility products.

The calculations show that most leachates tend to show saturation with calcite, dolomite, and rhodochrosite, implying that the Ca^{2+}, Mg^{2+}, Mn^{2+}, and CO_3^{2-} concentrations appear to be controlled by the precipitation of these mineral phases. The saturation with respect to the carbonate phases is caused by the high carbonate concentrations resulting from the generation of CO_2 during microbial degradation of organic matter. High Mn^{2+} concentrations are presumably a result of the reduction of manganese oxide phases during the anaerobic degradation process.

As expected, most leachates exhibit undersaturation with respect to gypsum. This is not surprising, considering that sulphate concentrations are low due to the bacterial sulphate reduction process. In the case of iron equilibria, all leachates are generally distinctly supersaturated with respect to siderite, pyrite, and iron monosulphides (amorphous FeS and mackinawite). Calculated supersaturations can be attributed to several factors: (a) Fe^{2+} is complexed by dissolved organic constituents; (b) the solubility products are incorrect; (c) other phases than carbonate formation are controlling Fe^{2+} concentrations. Consideration of other iron phases indicates that in several leachate samples, Fe^{2+} concentrations may be controlled by vivianite, a ferrous phosphate. However, other leachates show gross supersaturation with respect to the phosphate phases. It is quite conceivable that Fe^{2+} is complexed with chelating agents such as EDTA which has been reported to be present in most trench leachates. The net effect of iron complexation would be to suppress Fe^{2+} activity and to increase its solubility.

In summary, solubility calculations based on trench leachate compositions indicate that the calcite, dolomite, and rhodochrosite mineral phases are likely to form in the trench environments and exert control on the concentrations of Ca^{2+}, Mg^{2+}, Mn^{2+}, and CO_3^{2-}. In the case of iron equilibria, gross supersaturations are found with respect to siderite, mackinawite, amorphous FeS, and pyrite. Some leachates exhibit saturation with respect to vivianite.

5.2 Oxidation Behaviour of Anoxic Trench Leachates

Oxidation experiments performed by Dayal et al (1984) on several trench leachates provide insights into the behaviour of anoxic trench leachates as they encounter

a relatively less reducing environment along groundwater flow paths. This information is important considering that the sorption characteristics and solubilities of several radionuclides, especially the actinides, are significantly different in oxidizing and reducing conditions. Furthermore, the development of a geochemical discontinuity, represented by ferric oxyhydroxide precipitation, following oxidation of iron-rich anoxic leachates, can have a profound effect on the migration of radionuclides.

Laboratory experiments demonstrated that, upon oxidation, an anoxic trench leachate undergoes a series of geochemical changes that result in a drastically different solute chemistry. Some of the important changes included oxidation of ferrous iron and subsequent precipitation of ferric oxhydroxide, changes in alkalinity and pH, a drastic increase in Eh, and generally relatively little change in radionuclide concentrations.

Preliminary geochemical modelling of both anoxic and oxidized leachates was carried out by Dayal et al (1984). In this report, the modelling results of the oxidation of trench leachate 19s(81) are presented, showing the nature and extent of changes induced as a result of progressive oxidation with incremental addition of oxygen to the system. The composition of trench leachate 19s, which represents input data for our modelling effort, is presented in Table 5.1. Leachate oxidation is achieved by raising the PO_2 of the system. $Fe(OH)_3$(am) or ferric oxyhydroxide is allowed to precipitate at saturation, and, thereafter, the leachate is kept in equilibrium with the solid phase. Assumption of precipitation of ferric oxyhydroxide is reasonable considering that a reddish-brown precipitate was observed during the experiments and that the total dissolved iron decreased with increasing degree of oxidation (Dayal, et al, 1986).

Our modelling results are shown in Tables 5.2 and 5.3. The predicted changes in redox potential, pH, and total alkalinity with increasing degree of oxidation are compared with the laboratory observations reported by Dayal et al (1986). As shown in Fig. 5.2, our modelling predicts all major geochemical changes observed during the leachate oxidation experiments. Leachate 19s(81) is a high alkalinity, well-buffered system, with a large acid-neutralizing capacity. Oxidation of ferrous iron and subsequent precipitation of ferric oxyhydroxide will generate hydrogen ions and reduce the total alkalinity of the solution. Distinct changes occur at $PO_2=10^{-60}$atm. at which the solution reaches saturation with amorphous $Fe(OH)_3$. At this stage, the ferric oxyhydroxide will precipitate out. This is accompanied by a drastic decrease in total iron and alkalinity of the leachate. When oxidation exceeds the point where the redox potential, Eh = 200 mV, discrepancies are apparent between observed and modelled pH values. Modelling results indicate that, at this point, more than 99 percent of the initial iron had precipitated and no more dissolved iron is available for reaction. Therefore, both pH and alkalinity should be subject to little changes upon further oxidation. This discrepancy could be a result of the presence of organic carbon in the leachate (430 mg/l dissolved organic carbon) which was not considered in our modelling effort.

As shown in Fig. 5.3, the degree of saturation for carbonate minerals decreases with progressive oxidation. This is a result of decreasing carbonate content of solution with increasing degree of oxidation. For example, the saturation index for siderite changes from over- to under-saturation, reflecting oxidation

of the Fe^{2+} to Fe^{3+} ion and the corresponding generation of acidity which neutralizes the leachate alkalinity (CO_3^{2-}).

The direction and extent of the leachate 19s(81) oxidation reaction progress is best illustrated in the Eh-pH relationship diagram for the Fe-H_2O-S-CO_2 system (Fig. 5.4). The heavy broken line with an arrow represents the predicted evolution of leachate chemistry upon incremental oxidation of the solution. The anoxic leachate is initially in the iron sulphide/siderite stability field and, upon progressive oxidation, both the Fe^{2+} and CO_3^{2-} ions are consumed. This contributes to disequilibrium with respect to siderite and finally approaching saturation with respect to ferric oxyhydroxide, as reflected by the final extent of the oxidation reaction progress, based on both observed and predicted changes in leachate chemistry (Fig 5.4).

Table 5.1. Chemical Composition of Trench Leachate 19s(81) from the Maxey Flats LLW Disposal Site[a]

Constituents	Concentration (mg/L)
Ca^{2+}	49
Mg^{2+}	128
K^+	27
Na^+	231
Fe_T	65
Fe^{2+}	62
Mn_T	0.5
Si	b
NH_4^+	45
F^-	40
Cl^-	231
SO_4^{2-}	<2
DIC[c]	170
Alkalinity[d]	1040
pH 7.7	
EH -230mV	

[a] From Dayal, et al (1984)

[b] Not determined

[c] Dissolved inorganic carbon

[d] Reported as $CaCO_3$

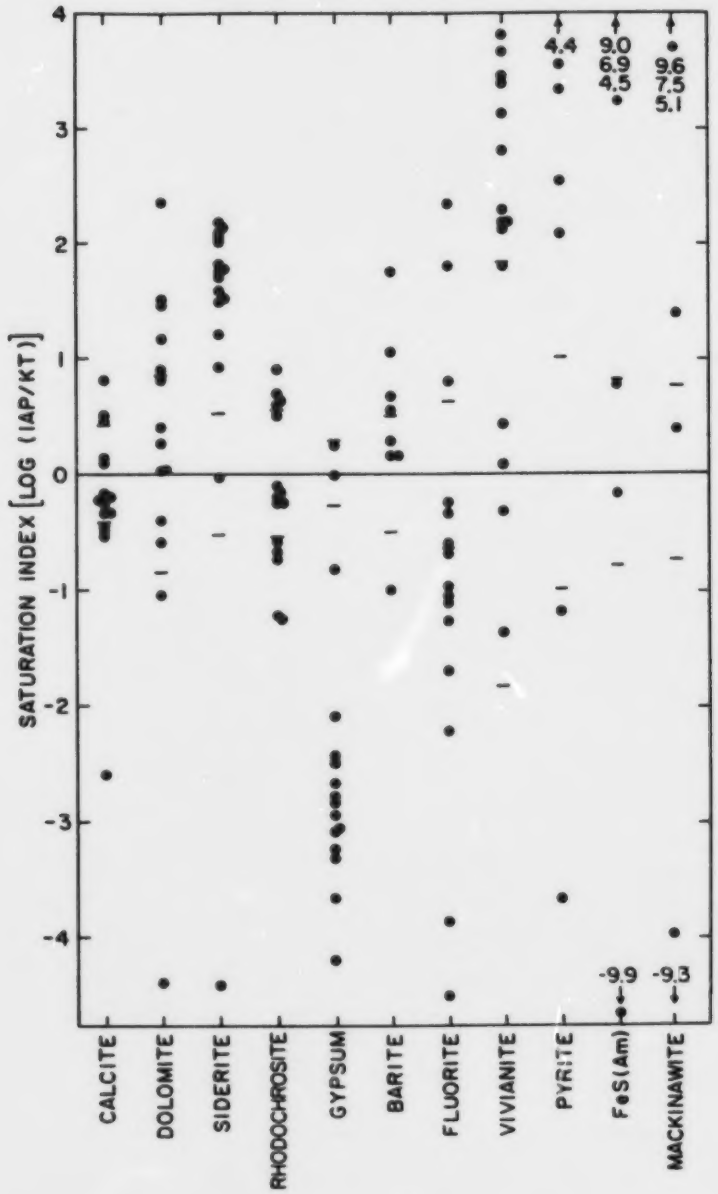


Fig 5.1. Calculated ion activity products for the major solutes in trench leachates compared to solubility products of selected minerals expected to form under anoxic conditions. The comparisons are made in terms of saturation index [Log (IAP/KT)]. Closed circles represent calculated saturation indices based on observed leachate compositions for the various minerals. Horizontal bars represent 5% tolerance limits on saturation indices due to uncertainties in the values of mineral solubility products (K_{sp}).

Table 5.2 Predicted Changes in Solution Chemistry Upon Incremental Addition of Dissolved Oxygen (PO_2) to Leachate 19s(81)

$\log PO_2$	pe	Eh	pH	Fe_T (mmol)	Fe(%)	Alkalinity (meq/kg)
-68.0[a]	-3.90[a]	-230.0[a]	7.7	1.17	100.0	21.8[a]
-65.0	-3.16	-186.0	7.7	1.17	100.0	21.8
-60.0	-1.92	-113.0	7.7	1.17	100.0	21.8
-55.0	-0.51	-30.0	7.5	0.57	48.7	20.6
-60.0	0.85	50.0	7.4	0.05	4.5	19.6
-45.0	2.11	125.0	7.4	0.01	1.1	19.5
-40.0	3.36	198.0	7.4	0.01	<1.0	19.5
-35.0	4.61	272.0	7.4	0.01	<1.0	19.5
-30.0	5.86	346.0	7.4	0.01	<1.0	19.5
-25.0	7.11	420.0	7.4	0.01	<1.0	19.5

[a]Represents initial dissolved oxygen of the leachate.

Table 5.3 Predicted Changes in Mineral Saturation Indices During Oxidation Of Leachate 19s(81)

log PO_2	SATURATION INDICES [LOG (IAP/KT)] Calcite	Dolomite	Siderite	Rhodochrosite
-68.0[a]	0.83	2.35	2.13	-1.00
-65.0	0.83	2.35	2.13	-1.00
-60.0	0.83	2.35	2.13	-1.00
-55.0	0.67	2.02	1.77	-1.01
-50.0	0.55	1.78	0.62	-1.01
-45.0	0.54	1.76	-0.62	-1.01
-40.0	0.54	1.76	-1.87	-1.01
-35.0	0.54	1.76	-3.12	-1.23
-30.0	0.54	1.76	-4.37	-2.29
-25.0	0.54	1.76	-5.62	-3.53

[a]Represents initial dissolved oxygen of the leachate.

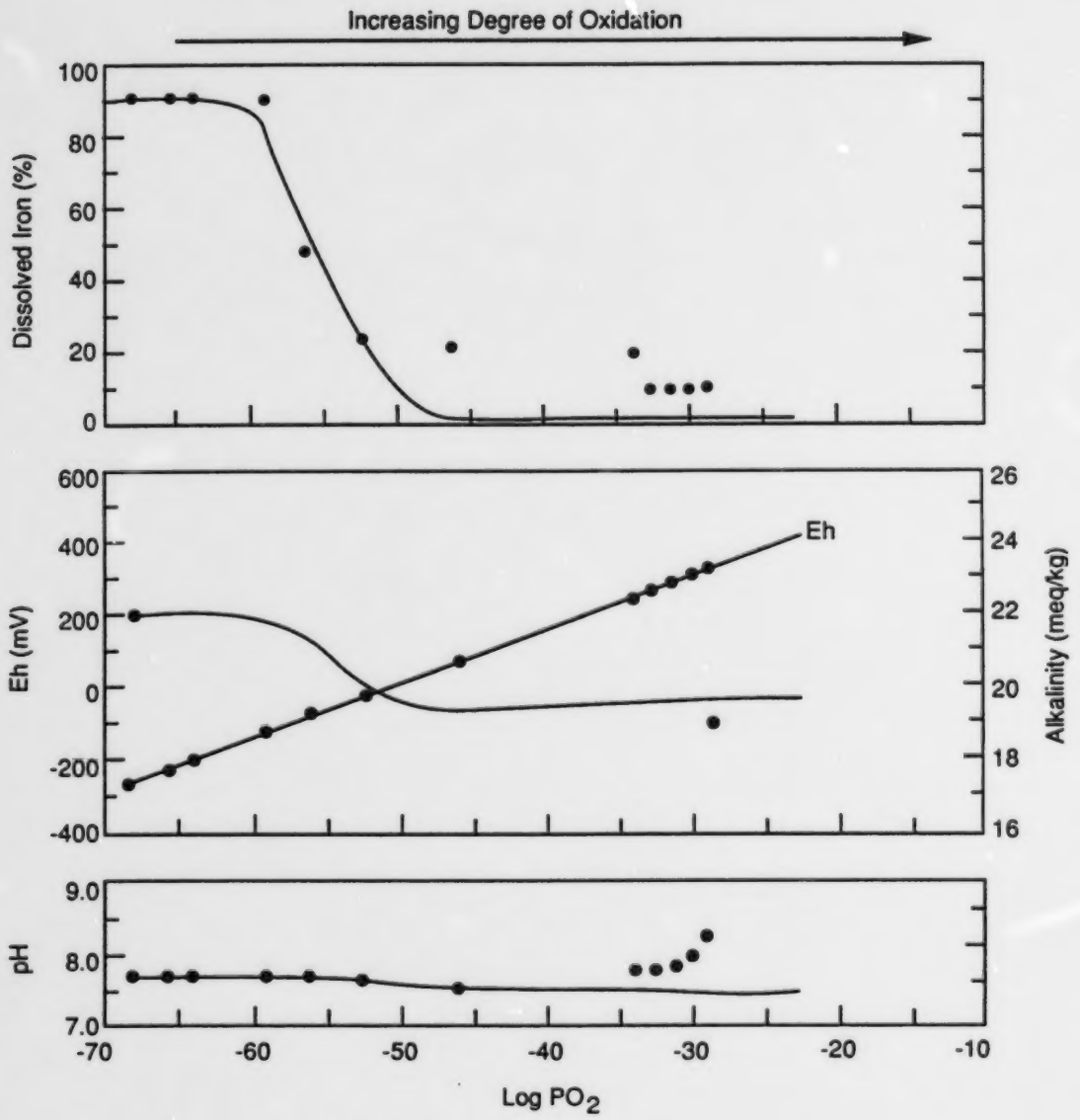


Fig. 5.2 Predicted (solid line) and observed (•) changes in anoxic leachate chemistry with increasing degree of oxidation.

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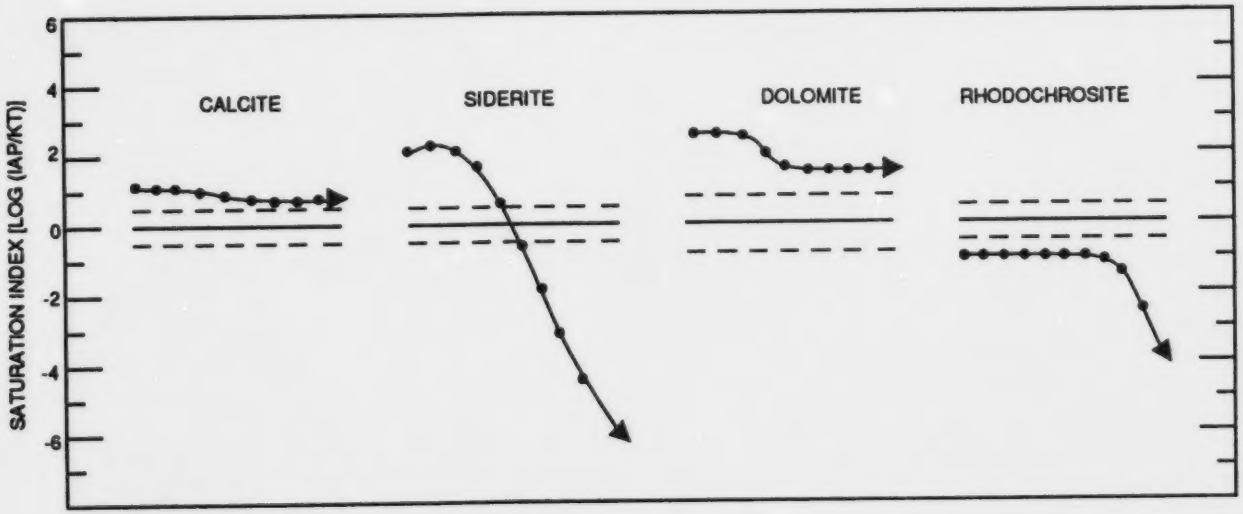

Fig. 5.3 Changes in carbonate mineral saturation indices with progressive oxidation of anoxic leachate. Arrows indicate the direction and extent of oxidation-induced changes. Dashed horizontal bars represent 5% tolerance limits on saturation indices due to uncertainties in the values of mineral solubility products (K_{sp}).

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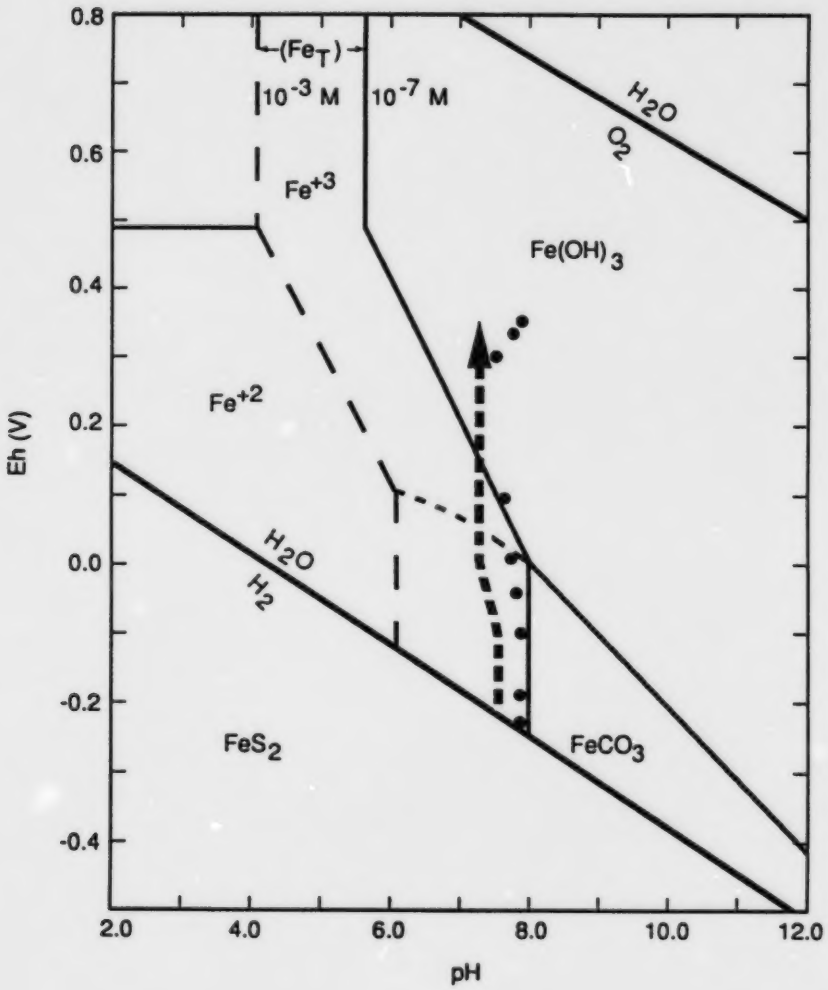

Fig. 5.4 The Eh-pH relationship for leachate 19s(81) reaction path and progress during oxidation (after Dayal et at., 1986). Dissolved Σ Fe = 10^{-3} M to 10^{-7} M; ΣCO_2 = 10^{-3} M; ΣSO_4^{2-} = 10^{-4} M. Both predicted (broken line) and observed (•) changes are illustrated.

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6.0 CONCLUSIONS

Computer modelling was performed to demonstrate the wide applicability of the computer program PHREEQE to diverse geochemical problems such as the evaluation of FGD waste leaching, leachate/clay liner interactions, bedrock gypsum dissolution as related to the R.H. Saunders G.S. dam safety program, grout carbonation for the C-14 isolation research program, and oxidation-induced changes in anoxic leachates from a low-level radioactive waste disposal site.

The modelling results of FGD waste dissolution indicate that the evolving leachate chemistry with time can be predicted. Furthermore, the computer simulations indicate that leachates will be highly alkaline, with solid phases exerting a strong control on leachate chemistry and that specific liner materials may be necessary to control leachate contamination of the ambient groundwater.

With respect to the gypsum dissolution problem, the results show that geochemical modelling can be used quite effectively to define the geochemical character of ambient groundwater; calculate the dependence of solubility, degree of undersaturation, and dissolution rate on solution chemistry; and evaluate the effect of varying redox conditions (S^{2-}/SO_4^{2-}) on gypsum and anhydrite solubility.

Modelling of laboratory grout/CO_2/water experiments designed to evaluate the efficiency and chemistry of C-14 uptake by cement-based materials provides important information on the reactions controlling the grout carbonation process, as well as on the evolving mineral assemblages that are likely to exert control on the changing water chemistry. Furthermore, the PHREEQE simulations have delineated the sequence of grout carbonation, providing important information on the degree of carbonation with incremental additions of CO_2 to the grout/water systems.

For the Maxey Flats low-level radioactive waste disposal site, the modelling results indicate that most anoxic leachates exhibit distinct saturation to super-saturation with respect to calcite, dolomite, and rhodochrosite. The saturation with respect to the carbonate phases is caused by the high carbonate concentrations resulting from microbially-mediated generation of CO_2 in the trenches. The results further indicate that PHREEQE can be used to simulate geochemical changes that are likely to occur as an iron-rich, anoxic leachate encounters a relatively less reducing environment. It is important to know the nature and extent of these near-field chemical changes because they have a direct effect on source term characteristics which are normally assumed to be time invariant.

Because of the wide applicability of PHREEQE to diverse geochemical problems, as demonstrated above, and the importance of the accompanying thermodynamic data base in addressing these problems, we plan to extend the application of PHREEQE to other relevant problems at Ontario Hydro such as the C-14 source term geochemistry, leaching of concrete for high integrity containers for the storage/disposal of reactor waste, fly ash leaching and disposal, and BNPD groundwater geochemistry.

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